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ELECTRONIC SPECTRA OF 1, 3, 5-TRIMETHYLBENZENE IN THE LIQUID STATE AND IN THE SOLID STATE AT – 180°C*

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ABSTRACT. The ultraviolet absorption spectra of 1, 3, 5-trimethylbenzene in the liquid and solid states have been analysed and the results have been compared with those reported by previous workers for the same substance in the vapour state and for other similar compounds in different states. The 0, 0 band, which is forbidden in the vapour state, is found to appear with moderate intensity in the spectra due to the liquid and the solid at –180°C indicating a distortion of the three-fold symmetry of the molecules owing to the influence of the surrounding molecules of the same type. It is pointed out that such a distortion takes place even in absence of any halogen atom in the molecule.

INTRODUCTION

Sponer and Stallcup (1948), while analysing the absorption spectrum of 1, 3, 5-trimethylbenzene in the vapour state, observed that the 0, 0 band was absent. They ascribed the first strong band at 37000 cm^{-1} to $0 \rightarrow 1$ vibrational transition coupled to the electronic transition and a much weaker band at 36041 cm^{-1} to such a coupling of $1 \rightarrow 0$ transition and thus found the position of the 0,0 band to be at 36557 cm^{-1}. They pointed out that as the molecule possesses the symmetry D_{3h}, the 0,0 band is forbidden.

Banerjee (1957) observed that in the spectrum due to 1, 3, 5-trichlorebenzene in the solid state at –180°C, the forbidden 0,0 band appears with weak intensity. This has been explained on the assumption that the symmetry of the molecule is partially destroyed due to the formation of weak bands between chlorine atom of one molecule and a hydrogen atom of a neighbouring molecule.

Roy (1957) studied the absorption spectra of solutions of 1, 3, 5-trimethylbenzene and 1, 3, 5-trichlorobenzene in different solvents and observed that in the former case when the molecule of the solvent contains a chlorine atom or an OH group, weak intermolecular bonds are formed so as to distort the symmetry of the molecule and the 0, 0 band appears with weak intensity. In the latter case, solvents with molecules containing hydrogen atoms showed greater influence to produce the 0,0 band.

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In the present investigation the absorption spectra of 1, 3, 5-trimethylbenzene in the liquid and solid states have been studied to find out whether the surrounding molecules of the same type exert any influence on the electronic state of the molecule so as to destroy its three-fold axis of symmetry

EXPERIMENTAL

Chemically pure sample of 1, 3, 5-trimethylbenzene (B.D H.) was distilled several times under reduced pressure.

The experimental set up was the same used in an earlier investigation by the author (Sen, 1955). Spectrograms were taken on HP3 films with Hilger E1 Quartz spectrograph having a dispersion 3 A.U per mm. in the region 2600 Å. Very thin films of thickness of the order of a few microns were required for the spectrum due to the liquid state, the time of exposure varying from 10 to 15 minutes. The spectrum in the solid state was photographed with one hour's exposure time. Iron arc spectrum was taken in each spectrogram as comparison. Microphotometric records were obtained with a self-recording microphotometer of Kipp and Zonen type The frequencies of the bands were measured using the microphotometric records of iron lines as in the earlier investigation (Sen, 1956) The slit width was 0.3 mm (= 15 cm^{-1}) in the region 2600 Å.

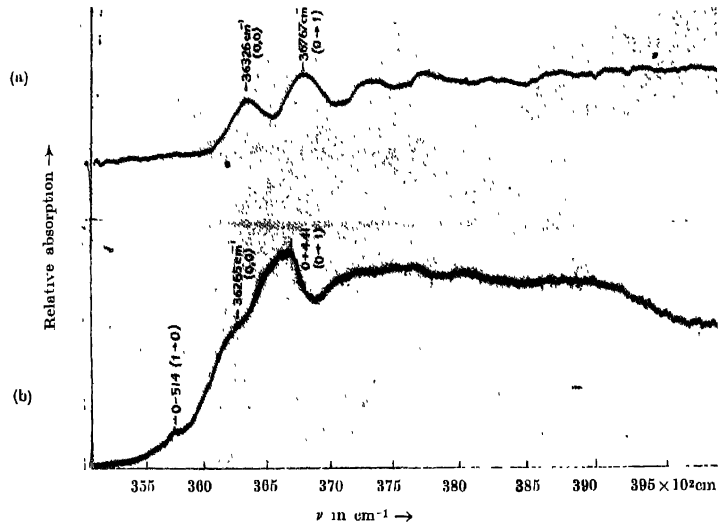

Fig. 1. Microphotometric records of the ultraviolet absorption spectra of 1, 3, 5-trimethylbenzene.

RESULTS

The microphotometric records of the spectra are reproduced in figure 1 and the wave numbers of the bands with approximate intensities and probable assignments are given in Table I.

DISCUSSION

It is seen from Table I that the first band at 36326 cm^{-1} due to the compound at −180°C is at a distance of 441 cm^{-1} from the next stronger band at 36767 cm^{-1}. In the spectrum due to the vapour state (Sponer and Stallcup, 1948) the distance between the first two bands is 959 cm^{-1}. These two bands were assigned to $1 \rightarrow 0$ and $0 \rightarrow 1$ vibrational transitions, the corresponding vibrational frequencies being 516 cm^{-1} and 443 cm^{-1} respectively. In the spectrum due to the solid state at −180°C, the first band at 36326 cm^{-1} cannot be due to $1 \rightarrow 0$ transition as there is no corresponding stronger band on the shorter wavelength side of the band at 36767 cm^{-1}. Hence the weaker band at 36326 cm^{-1} is to be assigned as the 0, 0 band and the band at 36767 cm^{-1} would correspond to the vibrational transition $0 \rightarrow 1$, the excited state vibrational frequency being 441 cm^{-1}. The band corresponding to the vibrational transition $1 \rightarrow 0$ corresponding to the ground state vibrational frequency 516 cm^{-1} is absent as the population of molecules at this frequency cannot be high in the solid state at −180°C. Further, in

TABLE I

Absorption bands of 1, 3, 5-trimethylbenzene in the liquid and solid states

Vapour (Sponer and Stallcup, 1948)	Solid at −180°C		Liquid at 30°C	
ν in cm^{-1} (Prominent bands)	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment
36041 (vw) (1, 0)			35751 (vw)	0−514 (1, 0)
36557 (calculated 0, 0)	36326 (s)	0, 0	36265 (w)	0, 0
37000 (s) (0, 1)	36767 (vs)	0+441 (0, 1)	36705 (s)	0+441 (0, 1)
37968 (s)	37288 (m)	0+962	37225 (m)	0+960
38300 (ms)	37724 (m)	0+962+441	37667 (m)	0+960+440
	38244 (m)	0+962×2	38185 (w)	0+960×2
	38688 (m)	0+962×2+441	38628 (vw)	0+960×2+440
	39210 (w)	0+962×3	39142 (vw)	0+960×3
	39645 (w)	0+962×3+441		

the spectrum due to the solid state at −180°C, progressions of $0+n\times962$ and $0+441+n\times962$ are observed while in the vapour state there is only the progression of $0+443+n\times968$. It is thus seen that the symmetric oscillation coupled to the 0, 0 electronic transition itself is allowed This shows that the three-fold axis of the molecule is not present in the solid state at −180°C and the 0.0 band is therefore not forbidden in the solid state.

The 0,0 band shifts in this case by 241 cm^{-1} towards longer wavelengths from the calculated position of the 0, 0 band due to the vapour state. The corresponding shifts observed in the case of benzene (Kronenberger, 1930) and 1, 3, 5-trichlorobenzene (Banerjee, 1957) are 261 cm^{-1} and 279 cm^{-1} respectively.

The spectrum due to the liquid state at room temperature exhibits system of bands, of which the first band at 35751 cm^{-1} is very weak and is at a distance of 514 cm^{-1} from the second band. The first band thus corresponds to $1\rightarrow0$ vibrational transition and the second band 36265 cm^{-1} can be assigned to 0,0 transition. This system of bands is thus shifted towards longer wavelengths with reference to the system due to the solid state by 61 cm^{-1}.

It is concluded from the above results that even when the molecules of 1, 3, 5-trimethylbenzene are surrounded by other molecules containing only CH_3 groups, the three-fold symmetry of the six π-electrons in the ring is disturbed and this influence is intensified when the liquid is frozen and cooled to −180°C. Such an influence is expected in the case of 1, 3, 5-trichlorobenzene from the usual chemical point of view, but the results of the present investigation furnish some evidence for the existence of the influence even in the case of the trimethyl compound

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REFERENCES

Banerjee, S. B., 1957, *Ind. J. Phys.*, **31**, 483.
Kronenberger, A., 1930, *Zeits. f. Physik*, **63**, 494.
Roy, S. B., 1957, *Ind. J. Phys.*, **31**, 588.
Sponer, H. and Stallcup, Mary Jane, 1948, Contribution a' l'Etude de la Structure Moleculaire (Deosoi, liege), p. 222.
Sen, S. K., 1955, *Ind. J. Phys.*, **29**, 561.
„ 1956, *Ind. J. Phys.*, **30**, 56.